ACTIVATED CARBONS FROM STEAM EXPLODED WOOD.

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Keywords: Activated carbon, Steam explosion, Porosity

INTRODUCTION

In a continuing experimental program, we are investigating the conversion of hardwoods, such as white oak (*Quercus alba*) to activated carbons by chemical activation with phosphoric acid[1-3]. The aims of the research are to establish the relationships between chemical and morphological change and porosity development, with the long term goal of developing new adsorbents with controlled porosity and surface chemistry, through the selection of the precursor, reagent, and reaction parameters. The research is further directed to enhancing the use of wood materials, some of which are not appropriate feedstocks for conventional industrial applications, and to providing potential solutions to the problem of the economic utilization of wood wastes from primary and secondary wood industries.

Our previous work on phosphoric acid activation has demonstrated that there is a direct correspondence between porosity development and a dilation of the altered wood structure that takes place at heat treatment temperatures above about 200-250°C [1]. While the mechanisms that lead to this structural expansion are unclear, it is clearly related to the effects of the reaction of phosphoric acid with the biopolymers in the wood, primarily lignin and cellulose. For example, compared to reaction in the absence of this reagent, phosphoric acid produces an increase in carbon yield that is attributed primarily to the retention of cellulose, albeit in altered form, through the promotion of crosslinking reactions. However, lignin and other biopolymers, also contribute to the pore structure. The most significant chemical changes seem to occur at low temperatures: ^{13}C NMR spectra show that by 50°C there is a loss of carboxyl and methyl groups from the lignin structure, and the carbohydrate (cellulose and hemicellulose) signature disappears by 100°C [4]. These findings correspond with observations that lignin appears to undergo partial digestion or depolymerization at low temperatures[1]. It has been reported in other work that wood transforms into a "plastic" state on heat treatment to low temperatures [5].

For these reasons, current studies focus on elucidating the roles of wood biopolymers upon activation with H_3PO_4, and how they influence the porosity of the carbon product. In this context, wood and wood fractions have been produced by a technique known as steam explosion, that has been combined with extraction methods to provide materials with a range of different compositional characteristics for the synthesis of activated carbons. Steam explosion of lignocellulosic biomass from agricultural and forest resources is a technology that was developed for converting woody resources not qualified for the production of paper pulp into constitutive biopolymers [6]. The results presented here will consider how the pore size distribution of the activated carbons is influenced by the severity of the steam explosion treatment and fractionation protocol.

EXPERIMENTAL

Materials and Materials Preparation

Quantities of white oak were supplied in the form of wood chips (3 x 2 x 0.5 cm) by Westvaco Corporation. The chips were subjected to steam explosion treatment at four severity levels in a pilot scale unit at the Virginia Polytechnic Institute (VPI). Samples of the products were then subjected to solvent extraction to provide a total of 17 starting materials with different compositional characteristics: the parent wood; the complete steam exploded product at four severities, and extracted fractions from each of these - insoluble fractions from water and alkali extraction and recovered lignin fom alkali extraction. A schematic of the steam explosion process and product separation scheme is shown in Figure 1.

The conditions used for steam explosion influence the chemical and molecular characteristics of the product and product fractions. A calculated severity parameter, log R_o, is used to denote the combined effects of time, temperature and steam pressure that are used in any particular treatment [7]. Differences in cell structure and in chemical structure are caused by varying the severity of steam explosion thus providing material of altered composition and microstructure.

Water extraction of the steam exploded wood fiber removes most of the hemicellulose. Alkali extraction creates a cellulose-rich fibrous fraction from which most of the lignin has been removed.

Extraction is accomplished using a liquor to wood ratio of 8:1, at a caustic charge of 15-20% of dry fiber, at 80 to 90°C for 30 minutes. Samples are then filtered, washed in a counter current mode and the solubles and insolubles are recovered. A lignin-rich fraction can be produced as a precipitate upon neutralization of the alkaline filtrate (approx. 90% lignin). By these procedures, the component biopolymers are isolated as xylose-rich water soluble solids; as cellulose-rich fiber solids; and as lignin-rich fraction by acid precipitation.

Chemical Activation

Activated carbons are synthesized by mixing an aqueous solution of phosphoric acid with the starting material, after first grinding the sample to produce a -100 mesh powder (to ensure good contact). The acid is added as an 85% solution in a volume such that the weight ratio of acid to as-received sample is 1.45 : 1.0. The mixture is then heat treated in two stages. First, low temperature heat treatment to 170°C for 30 min. under nitrogen flow to allow time for penetration of the reagent and to complete the initial reactions. This is followed by heating (again in flowing nitrogen) to a final temperature in the range 300-650°C, with a hold time of 1 hr. at maximum temperature. The product, after cooling, is then leached extensively with distilled water to pH 6 -7 to recover the reagent, before drying and further characterization.

Characterization

Information on the carbon pore structure was derived from nitrogen adsorption isotherms obtained at 77K on a Coulter Omnisorb 100CX apparatus. Surface areas were determined by the BET method. Micropore volumes (pores less than 2 nm diameter), W_0, were determined using the Dubinin-Raduskevich equation [8], and mesopore volumes (pores of diameter 2 to 50 nm diameter) were determined by the BJH method [9].

RESULTS AND DISCUSSION

One of the apparent effects of modifying the wood structure by steam explosion is that, compared to the parent wood, there is more visible evidence of reaction commencing at room temperature upon addition of the acid solution. This observation could be considered to be due to the opening of the wood structure by the steam explosion treatment, permitting increased access by the phosphoric acid. However, thermogravimetric analyses of samples of the parent wood and product from pretreatment at $\log R_o = 4.0$ have failed so far to show any significant differences in behavior on H_3PO_4 activation.

The micropore and mesopore volumes of activated carbons produced from the parent wood and from samples subjected to steam explosion treatment at different severities (without subsequent fractionation) are shown in Figure 2, together with the totals of these volumes. It can be seen that, even at the lowest severity, steam explosion causes an appreciable increase in total pore volume (excluding macropores, defined as > 50 nm diameter). Compared to the parent wood, steam explosion at $\log R_o = 4.0$ increases the total pore volume by about 30%. Most of this change is due to an increase in micropore volume, with an associated change in BET surface area from 1300 to 1950 $m^2.g^{-1}$, Figure 3. The result demonstrates that wood pretreatment by steam explosion can be very effective for producing structural changes that strongly influence the pore characteristics of the derived carbons.

As can be seen, with further increase in $\log R_o$ there is a progressive reduction in total pore volume, due to decreases in both micropore volume, as reflected by the changes in BET surface area shown in Figure 3, and in mesopore volume. The fact that the volumes in both pore ranges decrease together suggests that the effect of steam explosion severity on porosity is more complex than simply shifting the overall pore size distribution to larger or smaller pore sizes. It appears that, at high treatment severities, the wood structure is so extensively disrupted that the normal mechanisms by which phosphoric acid activation generates porosity begin to become appreciably impaired.

Further modifications to the steam exploded wood samples were effected by the solvent extraction scheme described earlier to produce: water-insoluble fractions; alkali-insoluble fractions; and lignin-rich fractions recovered from the alkali-solubles by precipitation. The pore structural parameters of activated carbons produced from these precursors, at the different levels of steam explosion severity, are summarized in Table 1: micropore volume, mesopore volume, and BET surface area -note that macroporosity is not included.

Although the reproducibility of these preliminary experiments has yet to be confirmed, certain trends can be tentatively identified. For the series of carbons produced from the water-insoluble fractions, the micropore volumes appear to be insensitive to $\log R_o$, over the range studied, while there is a a reduction in mesopore volume with increasing severity. The alkali-insolubles produce carbons with lower microporosity, but here the mesopore volume increases with severity. The data indicate that mesoporosity passes through a maximum, but in any case very high mesopore volumes have been measured at high severities. Carbons with these characteristics would be suitable for liquid phase applications, where wider pores are desirable from the standpoint of being able to accommodate large molecules, and to facilitate diffusion of the adsorbate through the liquid in the pores.

The lignin-rich fractions produced carbons with micropore volumes similar to those in the carbons from the alkali-insolubles, and again were unaffected by severity. However, the mesoporosity was reduced to low values at steam explosion severities greater than 4.0.

SYNOPSIS

The principal outcome of this research to date is that it has demonstrated that the techniques of steam explosion and solvent extraction allow the production of substantially different materials from a single wood type, and that these materials can function as precursors for the synthesis of powdered activated carbons possessing a range of pore structural characteristics. For example, low severity steam explosion can be used to increase the micropore volume and surface area and produce a carbon that would be more suitable for the adsorption of small molecules, typical requirements for gas phase adsorption. In contrast, high severity steam explosion followed by isolation of the alkali-insolubles can produce a carbon with high mesopore volume, suitable for liquid phase applications. The differences between these materials are clearly illustrated by the nitrogen adsorption isotherms in Figure 4: whereas adsorption on the predominantly microporous carbon approaches a plateau at a relative pressure above about 0.3, adsorption on the mesoporous carbon continues to rise due to the filling of wider pores.

In future work, further studies will be made to establish links between precursor composition and the properties of the powdered activated carbons, and investigations will be made of the feasibility of producing extruded activated carbons from these same precursors.

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ACKNOWLEDGEMENT

The authors would like to thank the US Department of Agriculture, Contract #93-02345, Program Director: Dr. Charles Cleland, and University of Kentucky, Center for Applied Energy Research for financial support.

Table 1: Micro- and mesopore volumes and BET surface areas of activated carbons from fractions of steam exploded wood.

Severity	Steam Exploded	Water Extracted	Alkali Extracted	Lignin
Micropore volume(cc/g) [*Parent wood 0.51 cc/g]				
4.01	0.77	0.76	0.60	0.56
4.26	0.67	0.73	0.42	0.58
4.35	0.7	0.75	0.44	0.59
4.43	0.59	0.77	0.60	0.57
Mesopore volume(cc/g) [*Parent wood 0.34 cc/g]				
4.01	0.36	0.41	0.21	0.56
4.26	0.44	0.26	0.45	0.13
4.35	0.26	0.22	1.07	0.14
4.43	0.25	0.18	0.69	0.17
BET surface area(m^2/g) [*Parent wood 1300 m^2/g]				
4.01	1945	1920	1408	1697
4.26	1589	1746	1166	1327
4.35	1691	1789	1314	1369
4.43	1413	1792	1734	1328

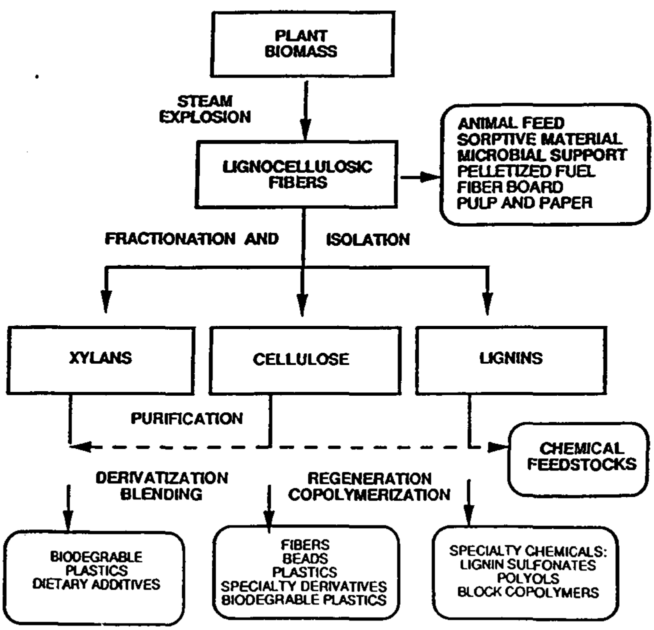

Figure 1: Schematic for separation of biomass into constituent polymers (Biobased Materials Center, Virginia Polytechnical Institute)

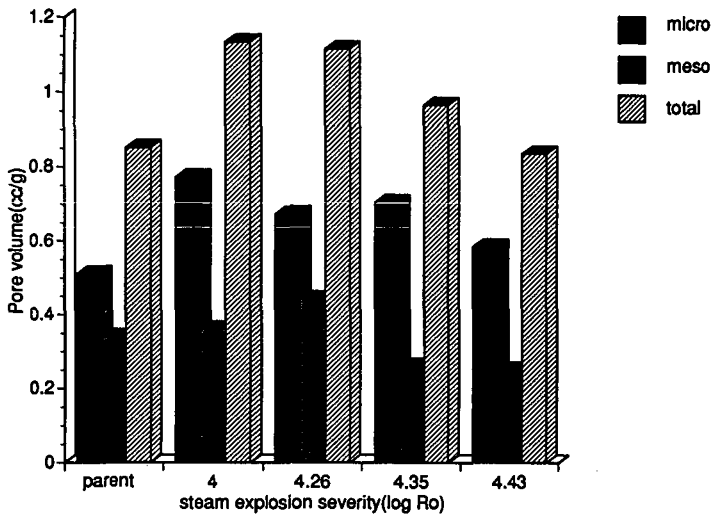

Figure 2: Influence of steam explosion severity on porosity of activated carbons (H_3PO_4 activation).

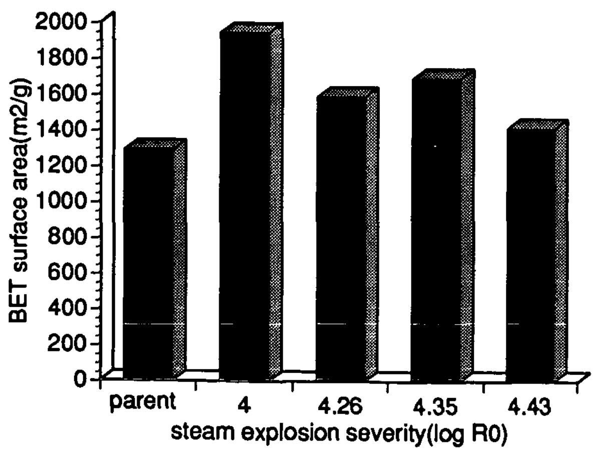

Figure 3. Influence of steam explosion severity on BET surface area of activated carbon (H_3PO_4 activation).

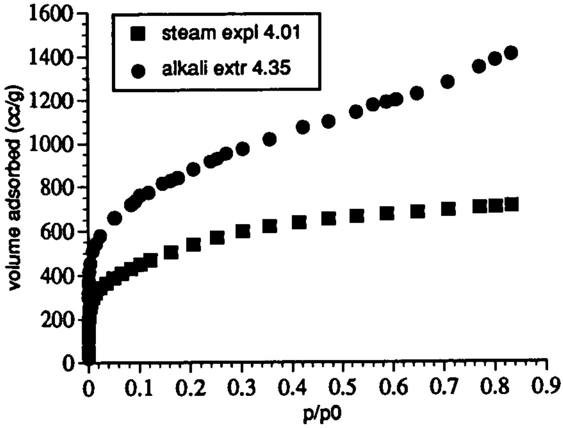

Figure 4. Nitrogen adsorption isotherms (77K) of activated carbons. (precursor materials derived from white oak)